

33p.

N64 13927

UNPUBLISHED PRELIMINARY DATA

CODE-1

(NASA-CR-55330)

THERMODYNAMIC PROPERTIES OF CRYOGENIC FLUIDS

By

(Colo. U.)

R. B. Stewart and K. D. Timmerhaus

1963

33p

Orig

Cryogenic Engineering Laboratory

National Bureau of Standards

Boulder, Colorado

6033005

(NASA-CR-55330; NBS Paper A-3; R-295)

OTS: \$3.60 ph, \$1.19 mf

Presented at

Preprint of Paper No. A-3 prepared for presentation at the
1963 Cryogenic Engineering Conference at the University of
Colorado in Boulder, August 19 through 21.

U₂

12-21 Aug. 1963

2nd

Submitted for publication

OTS PRICE

XEROX \$ 3.60 ph
MICROFILM \$ 1.19 mf

Preliminary information
not released for publication

□ conf

Copies of this preprint can be obtained from the Cryogenic
Data Center, National Bureau of Standards, Boulder, Colorado

(Price 1.75)

M
fo

ABSTRACT

13927

To provide tabulations of thermodynamic properties for advanced cryogenic systems design, CEL-NBS has undertaken a re-evaluation of the pertinent experimental data. Tables and graphs of properties, as well as analytic functions for computer programming, are now available for several of the cryogenic fluids. These tabulations are intended to provide the engineer with comprehensive and consistent sets of data which are hopefully the best representation of the existing experimental data.

These compilations have also served to define the limitations of the existing data and to define the needs for new measurements. This paper summarizes the experimental data for the several cryogenic fluids and outlines some of the procedures utilized in providing the various sets of thermodynamic property values.

AUTHOR

CASE FILE COPY

THERMODYNAMIC PROPERTIES OF CRYOGENIC FLUIDS

R. B. Stewart and K. D. Timmerhaus*
CEL National Bureau of Standards
Boulder, Colorado

INTRODUCTION

The need for new tabulations of thermodynamic property data providing consistent values from cryogenic to ambient temperatures and extending to high pressures was recognized several years ago at CEL-NBS. As a consequence, a program was undertaken which has presently resulted in the publication of tables of properties for helium, normal hydrogen and nitrogen.

This compilation of thermodynamic data from the literature has been continued and in a few months new publications with tabular values will be available for oxygen, argon, neon and carbon monoxide. These publications will indicate the experimental data considered, the compilation methods and the estimated accuracy of these tabulations.

In yet another facet of this program, the experimental determination of thermodynamic data has also been undertaken. This program was initiated to measure the density, velocity of sound, viscosity, dielectric constant, thermal conductivity and constant volume specific heat of parahydrogen. As a result, new data on hydrogen are now available which have a high degree of precision and accuracy. A paper summarizing this work has been submitted for publication. The experimental program is still in progress and will be extended to other cryogenic fluids.

It is the purpose of this paper to review briefly the availability of cryogenic data for several fluids, to describe the evaluation and

* Also with the University of Colorado

13927 *one*

13927

compilation programs at this laboratory that have produced new property tables for these fluids, and to indicate the needs for new measurements. In describing the results of these compilation efforts, methods for utilizing the computer for thermodynamic data analysis are also suggested.

Author

P-V-T AND SPECIFIC HEAT DATA USED IN GENERATING THERMODYNAMIC PROPERTY TABLES FOR CRYOGENIC FLUIDS

In the design and analysis of systems in which the behavior of the fluid governs the physical parameters of that system, the accuracy to which the thermodynamic properties of the fluid are known is of paramount importance. An understanding of the possible limitations on the accuracy of property data is therefore demanded from the user of this data. Too often such tables are regarded as being on a par with mathematical tables and the uncertainty of these thermodynamic values are ignored in determining the probable variance between design predictions and the anticipated performance of a system*.

A review of the thermodynamic relations for calculating entropy and enthalpy, a description of the experimental data needed for calculating these thermodynamic quantities and illustrations of the adequacy with which these tabular values define the properties at cryogenic temperatures is an appropriate beginning for this review.

The "TdS equations", (1), (2) and (3), express possible paths of integration which may be considered for entropy determinations from a specific datum state to any arbitrary state in a P-V-T network.

*An excellent treatise which explores many facets of data evaluation is contained in an address by P. W. Bridgman [1].

$$TdS = C_v dT + T (\partial P / \partial T)_v dV. \quad (1)$$

$$TdS = C_p dT - T (\partial V / \partial T)_p dP \quad (2)$$

$$TdS = C_v (\partial T / \partial P)_v dP + C_p (\partial T / \partial V)_p dV. \quad (3)$$

Thus, information required for the calculation of tables of entropy include P-V-T data, either the derivative, $(\partial P / \partial T)_v$ or the derivative, $(\partial V / \partial T)_p$, and appropriate specific heat data. It should be noted in particular that the isothermal derivative, $(\partial P / \partial V)_T$ is not used in these property calculations, although P-V-T measurements are made along isotherms. Values of enthalpy may then be calculated by the relation,

$$dH = TdS + VdP \quad (4)$$

With few exceptions, thermodynamic property tabulations are calculated from P-V-T measurements and from zero pressure specific heat values derived from spectroscopic measurements. It should be noted that the zero pressure (or ideal gas) specific heat values, C_p^0 , are generally known with an uncertainty of less than 3 parts in 10,000 whereas the random deviations of the P-V-T data indicate uncertainties on the order of 2 to 5 parts in 1000. The phase boundaries involve a further complication and consequently must be defined by additional experimental data. As a minimum requirement, measurements of the vapor pressure are sufficient for the calculation of thermodynamic property differences due to a phase change. This is indicated by the Clapeyron equation, which may be expressed as,

$$\frac{dP}{dT} = \frac{S'' - S'}{V'' - V'} \quad (5)$$

where the prime notations are used to represent properties of different phases at the same temperature. The specific volumes at the saturation boundaries are then predicted by the P-V-T data of the adjoining phase and the vapor pressure. The accuracy of the physical measurements involved in adequately defining the two phase boundaries are such however, that it is necessary that other measurements such as specific heats at constant saturation for the liquid, latent heats and the saturation densities for both phases are also needed.

Other relations which should be reviewed are the equations relating changes in specific heats along the P-V-T network. These relations,

$$(\partial C_V / \partial V)_T = T (\partial^2 P / \partial T^2)_V \quad (6)$$

$$(\partial C_P / \partial P)_T = - T (\partial^2 V / \partial T^2)_P, \quad (7)$$

illustrate that the variations of the specific heats are functions of the second derivatives of the P-V-T surface. Thus, to compare P-V-T values for consistency with measured values of the specific heats requires extreme precision and accuracy even by present standards. Unfortunately, users of thermodynamic tables are often obliged to determine C_P and C_V variations from the entropy or enthalpy tabulations. This is a procedure which should be done only with due consideration of the uncertainties which are involved. Other thermodynamic relations which involve data that can be measured directly, such as velocity of sound and Joule-Thompson data, provide additional means of compiling thermodynamic tables and comparing the accuracies of these measurements.

The P-V-T data that have been measured for the cryogenic fluids are summarized below. This discussion is limited to the fluid

state and temperatures above the triple point of each fluid to 300°K. The data sources may be obtained from the bibliographies of the references cited.

1. Helium [2, 3] Although a considerable amount of new data have been published for values below 20°K, very few new measurements have been reported in the temperature range 20° to 300°K in the past 35 years. All of the published helium data from 20° to 100°K are for pressures below 100 atm while all data below 20°K are limited to 140 atm. More precise data, particularly at temperatures above 20°K and at higher pressures are needed. The many uses of helium over the entire temperature spectrum, and extending to very high pressures indicate a growing need for additional measurements.

2. Normal Hydrogen [4, 5] The information on the properties of hydrogen are probably sufficient for present needs. Measurements for the liquid and for gaseous hydrogen to room temperature with pressures to 200 atm became available from the Ohio State University Laboratory about ten years ago. New measurements from the van der Waals Laboratory in Amsterdam were published in 1959 for temperatures from -175° to 150°C. In addition, recent measurements for parahydrogen by CEL may be used to calculate normal hydrogen data from the triple point to 100°K. At this time, however, no comprehensive evaluation and compilation of all of these data have been included in published tabulations of normal hydrogen properties. The references cited consider only the older data, most of which were measured over 30 years ago and are not of the same order of precision and accuracy as some of the more recent data.

3. Parahydrogen [6, 7, 8, 9] Recent measurements should be adequate for the range from the triple point to 100°K with pressures to 340 atm. The data above 100°K, which is based primarily on normal hydrogen should be reevaluated and the newer data for normal hydrogen, indicated previously, included in a new calculation of the higher temperature values.

4. Neon [10, 11, 12] The data for low temperature neon is confined to temperatures above 55°K and pressures between 20 and 90 atm and to some saturation data. Uncertainties in this data suggest an experimental reevaluation for this range is desirable. Property values have been calculated using this existing data with suitable theoretical considerations for values down to 25°K with pressures to 200 atm; however, these values should be regarded only as interim data until new measurements can be made in a comprehensive experimental program.

5. Nitrogen [13] Although there have been several papers reporting experimental data for nitrogen, the existing data are not at closely spaced temperatures intervals, and in particular there are few data points for the liquid at high pressures. Nevertheless, the data do cover a range of temperatures from 75° to 300°K with maximum pressures of 3500 atm. Authoritative compilations of property tables have been made; however, the importance of accurate data for nitrogen should be emphasized. In addition to the many applications and systems employing nitrogen as a working fluid, the nitrogen data have also served as a model from which thermodynamic data have been generated for oxygen, neon, carbon monoxide and many other fluids.

6. Oxygen [14] The recent publication of liquid oxygen data from two independent sources has been a significant addition to the information on oxygen. Previous to the publication of this liquid data, the only significant experimental data were for saturated liquid and for gaseous oxygen, measured prior to 1925. The liquid data are still limited in pressure to 250 atm, and the gaseous data to about 60 atm. Oxygen properties have been deduced by corresponding states theory using nitrogen as a model which has been demonstrated to be fairly satisfactory. However, the new liquid data are in disagreement by as much as 0.7% in density values and although a consistent set of values can be obtained by a somewhat arbitrary evaluation, the uncertainty of this liquid data will remain at least 0.7% until new measurements are made. The gaseous data compiled from the experimental data as well as from the reduced nitrogen model can be regarded with some confidence, but as more precise property values become necessary, new measurements will definitely be needed. In view of some of the recent design considerations for oxygen pumps and tankage, data to very high pressures for the liquid as well as above the critical temperature would be very useful.

7. Carbon Monoxide [15] There are less experimental data for this fluid than any of the cryogenic fluids discussed. These data are limited to temperatures above 200°K and a few values at saturation. Property values have been calculated, however, using this existing data and the theory of corresponding states with nitrogen as a model for values down to 70°K with pressures to 300 atm. In view of the low interest in this fluid generally expressed by members of the cryogenic industry, however,

these calculated values may be sufficient for some time.

8. Argon [16] There appears to be a large quantity of experimental data for argon in the literature covering the entire temperature range for both liquid and vapor. This is probably a result, primarily of the interest of European physicists in a simple monatomic molecule and the relative unavailability of helium in Europe. A current program at CEL-NBS for evaluating and compiling this data should provide a comprehensive tabulation of the properties of argon. It is still too early in this program to indicate any current needs for additional measurements. However, as a model for studying the behavior of fluids, the properties of argon should be given considerable attention.

With the exception of the new data on parahydrogen, the definition of the various P-V-T surfaces appears meager, and for neon and carbon monoxide these surfaces are almost undefined. This is clearly demonstrated when a comparison of the experimental pressure and temperature data is made with the broad ranges of pressure and temperature for which thermodynamic properties have been tabulated.

EVALUATION OF THERMODYNAMIC DATA

The ideal of any data evaluation is to determine, for a particular parameter, the "correct" values. Where a vast amount of numerical material is available and where many experimenters, using different and sometimes dissimilar equipment have contributed, this ideal may be approached. In the case under discussion, however, it is not often that data from different sources even exist in a similar area, and in those instances where comparable data are available, there are

generally few opportunities for what may seem to be a conclusive selection. Even under the best conditions, the assessing of the probable excellence of measurements is a human undertaking and is thus limited to the best opinion of qualified experts. Various methods of evaluating the probable errors and determining the probable numerical values have been suggested. In most cases these methods involve the taking of weighted averages, with some scheme which considers not only the personal judgement of the evaluator, but even such factors as national prejudices. Averaging of the data treats all data values as being slightly in error but assumes that all measurements tend to be distributed around the correct value. The selection of "best values", that is, the selection of a particular set of data, is another approach which is sometimes justified but which remains a human enterprise subject to the same hazards as selection by weighted averages.

Another problem in the evaluation of data is the consideration of whether the parameter is capable of being precisely defined. The measurements considered here are, of course, generally limited by the present status of instrumentation development. It has also been a historical fact that as the accuracy of these physical measurements is increased that instead of attaining the correct value of a property, new sources of variations appear. This implies that physical measurements involve an element of theory and that the present status of this theory is another limitation in obtaining correct values. The recognition of the ortho-para modifications of some liquids is an example of this.

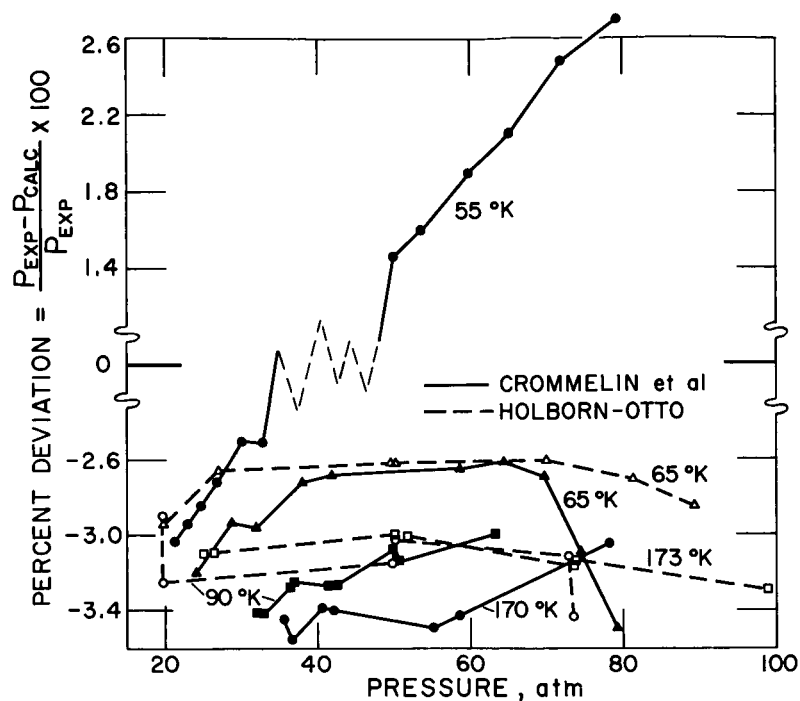
A few examples will hopefully serve to illustrate several techniques that have been employed in the evaluation of experimental data and the selection of "best values." These examples are taken from some of the work in the present CEL-NBS compilations of fluid

properties. In these evaluations, the character of the experimental data and the theoretical considerations of expected behavior based on studies of similar fluids have primarily influenced the data selection. Certainly the reputation of the various laboratories and particularly those of the individual experimenters can be implied as having had an effect on the selections.

One of these current problems is the selection of P-V-T data for liquid oxygen. Two recent independent publications of liquid density data, by van Itterbeek and Verbeke [17] and by Timrot and Borisoglebskiy [18], have been shown to be in disagreement by as much as 0.7% in the temperature range common to both sets of data. On examination of a graph illustrating the Timrot data, however, it has been observed that only 7 of their measurements were made in the temperature interval (70° to 93°K) covered by van Itterbeek. The remaining data by Timrot include 177 values in the temperature interval from 112° to 158°K. Timrot presents only a table of smoothed values so that no evaluation can be made of the individual measurements. In the compilation now in progress at this laboratory the liquid density values below 110°K reported by Timrot have been excluded; Timrot's data from 112° to 158°K together with the van Itterbeek data from 56° to 90°K then appear to be consistent. There is no firm basis for eliminating Timrot's low temperature values other than the scarcity of their measurements in this range, the unavailability of their raw data for comparison with their smoothed curve and the raw data of van Itterbeek, and the implication that their extrapolation to lower temperatures is in error since it is not supported by van Itterbeek's measurements.

A comparison of these two independent sets of data to values generated by application of the theory of corresponding states to a nitrogen model was not instructive in confirming either set of data, since the calculated values could not be made to agree with either set within the percentage variation existing between the two. The data are not sufficiently definitive for a more rigorous evaluation; however, with the elimination of Timrot's data below 110°K, consistent property tables can be generated and an indication of the probable uncertainty can be given to guide the user in assessing the effect of this uncertainty in his calculations. In the absence of more conclusive arguments, this range of uncertainty should include all of the Timrot data.

Another example is taken from the evaluation task for the density of neon. The experimentally determined P-V-T data for neon at low temperatures consist of two sets of data; one set is by Crommelin, Martinez, and Onnes [19] with data points from 55°K to ambient temperatures, and the other set is by Holborn and Otto [20, 21] from 65°K to ambient. In the range of values measured by both laboratories, the agreement may be considered as satisfactory. This is illustrated by Fig. 1 which compares the measured pressures to calculated values. The coefficients for the equation of state used in this comparison were derived with the van der Waal theory of corresponding states using argon data for a model. Even though systematic deviations are apparent between the argon and neon P-V-T surfaces, this does illustrate the general conformity between these two sets of data. The 55°K data, however, are conspicuously different in character with the other isotherms. The calculated values represent the predicted character of the P-V-T surface for neon. As a result, this variance at 55°K above 40 atm has been concluded to indicate that Crommelin's



B- 41597

Fig. 1 Deviation of the neon-argon
P-V-T surfaces by the law
of corresponding states

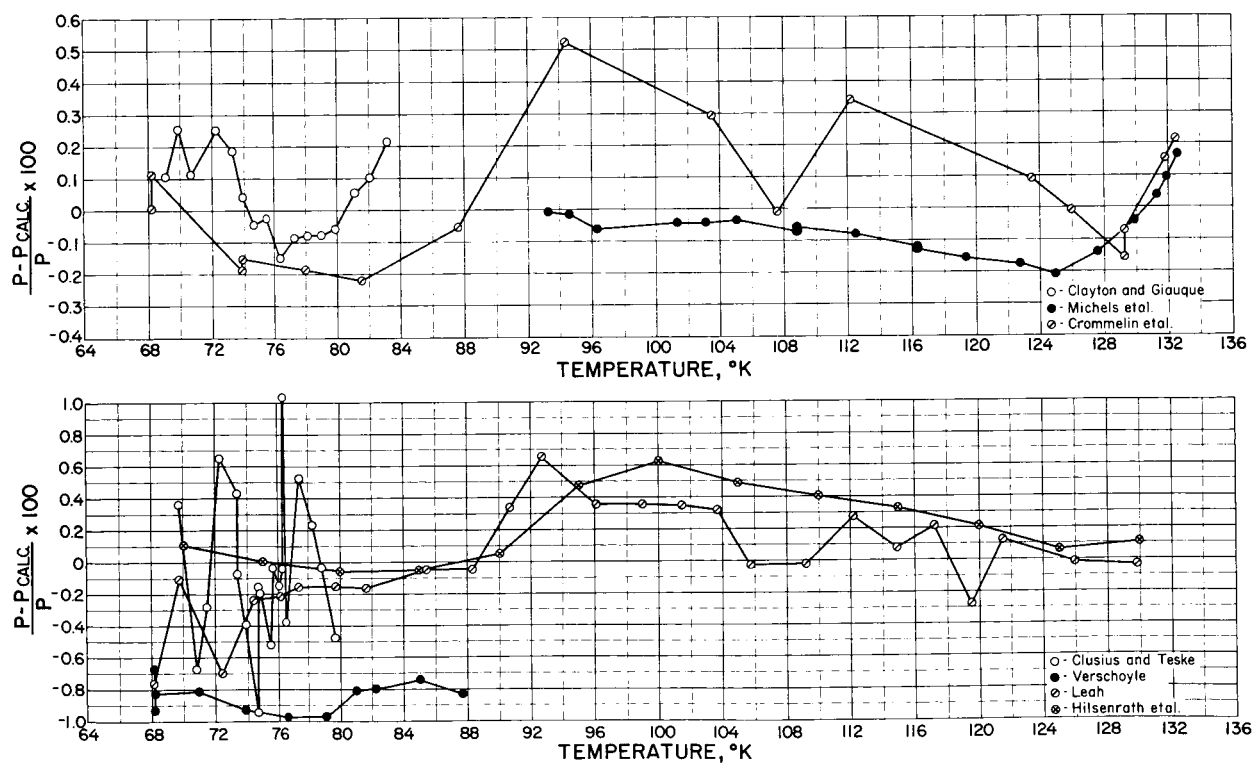


Fig. 2 Deviation of vapor pressure data for carbon
monoxide from calculated values in [15]

B- 41600

measurements at this temperature have a systematic error and should be disregarded in tabulating properties for neon.

A final example of data selection is taken from the task for the compilation of the properties of carbon monoxide. To aid in the selection of the most probable vapor pressure, the experimental data were illustrated as in Fig. 2. Values from the correlations by Leah [22] and Hilsenrath [23] are also included. The calculated values in this figure were obtained from an empirical equation with coefficients determined by a least squares fit of the data by Clayton and Giauque [24], Michels' et al. [25], and Crommelin et al. [26]. This selection represents an average of these "selected data". The data of Clusius and Teske [27] appear to be in agreement with the calculated values, but the precision of this data as indicated on Fig. 2 is such that it was not considered. The data by Verschoyle [28] differ by a constant factor from the data by Clayton and Giauque and Crommelin et al. and were therefore not considered for the selected data. The Leah and the Hilsenrath tabular values are both essentially in agreement with Crommelin et al. whereas the CEL-NBS tabular values include the more recent data by Michels et al.

These examples are somewhat illustrative of the decisions which confront the compiler. Much care has gone into the form of the comparisons and what may appear to be arbitrary is based on many intangible factors as well as the ones expressed here.

TECHNIQUES FOR PREDICTING PROPERTY DATA

One of the most powerful tools for predicting properties of a fluid is the theory of corresponding states, which relates the properties of similar fluids by suitable reducing factors. For example, the P-V-T surfaces of similar fluids are, by this theory, assumed to be

of similar shape. According to the van der Waal principle of corresponding states the critical point may be used to define the reducing parameters to scale the surface of one fluid to the dimension of another. Modifications of this principle, as suggested by Kamerlingh Onnes, have been used with some success to improve the correspondence particularly at low pressures. In practice then, this theory may yield some useful approximations and many modifications have been reported in the literature which offer improvements in the correspondence of various fluid property surfaces. As an example, it is suggested from Fig. 1 that the variation between the argon and neon surfaces is nearly constant from 55° (below 33 atm) to 170°K. One such modification has been applied [12] in predicting neon data by corresponding states theory to not only correct this displacement but also to reduce the systematic deviations between the neon and argon P-V-T surfaces. The use of molecular reducing parameters by deBoer [29] has given rise with some success to a host of correlations using this technique. The molecular theory has been found to be particularly useful for those low temperature fluids where quantum effects are known to have influence. A paper presented in another session of this conference is a good example of an application of this theory to transport properties [30] and work is well underway at this laboratory using molecular parameters to compare the surface tension data and the saturation properties for most of the cryogenic fluids.

More complex treatments which recognize the similarity of fluids and their PVT properties, for example, are contained in the literature in papers reporting generalized equations of state which may be applied to various classes of fluids. These generalized equations ordinarily allow for the adjustment of the P-V-T surface by providing for the introduction of several parameters. An equation of

this type is the generalized equation reported by Hirschfelder, Buehler, McGee and Sutton [31]. This particular equation allows for departures from the principle of corresponding states by introducing two additional correlating parameters, the slope of the reduced vapor pressure curve at the critical point and the critical compressibility factor. This equation is actually three separate functions for three different regions of application, including the liquid, high density fluid and low density gas regions. Another generalized equation of state that has been used at this laboratory is the Martin-Hou [32] equation of state.

In addition to the generalized equation of state, there are several multi-coefficient equations of state that are reported in the literature and which have found extensive use in work of this nature in the past several years. These equations, however, require a large amount of data in the range of interest for the determination of the coefficients. The Beattie-Bridgeman equation of state is a useful equation of this type and provides an excellent representation of the P-V-T surface in certain limited regions. Another more recent equation that is an improvement on the Beattie-Bridgeman is the Benedict-Webb-Rubin equation of state. Yendall [33] has also used an interesting equation for neon which may be represented by a simple summation. These equations, however, are not generally valid at higher densities, which is a rather severe restriction for many cryogenic systems. An equation which provides a better "fit", even to high densities is a modification of the B-W-R equation with 16 adjustable coefficients presented by Strobridge [13]. It is this latter equation of state which has been used extensively in the recent CEL-NBS compilations of the thermodynamic properties of helium, parahydrogen, neon, nitrogen, oxygen, carbon monoxide, and argon.

This equation is

$$\begin{aligned}
 P = & RT\rho + (RN_1T + N_2 + N_3/T + N_4/T^2 + N_5/T^4)\rho^2 + (RN_6T + N_7)\rho^3 \\
 & + N_8T\rho^4 + \rho^3(N_9/T^2 + N_{10}/T^3 + N_{11}/T^4)e^{-N_{16}\rho^2} \\
 & + \rho^5(N_{12}/T^2 + N_{13}/T^3 + N_{14}/T^4)e^{-N_{16}\rho^2} + N_{15}\rho^6.
 \end{aligned} \tag{8}$$

The application at this laboratory of this equation to several cryogenic fluids serves as an example of the problems of a P-V-T representation for thermodynamic data compilation. These applications are summarized as follows:

1. Helium [2] The helium data required minor modifications in (8). The result was a representation of the P-V-T data from 3° to 300°K for pressures to 100 atm, including both liquid and vapor phases. An area from 5° to 6°K for pressures greater than the critical pressure, however, could not be satisfactorily represented by this equation and graphical interpolations were required.
2. Parahydrogen [6] To make the results of the measurement program on the properties of parahydrogen at CEL-NBS more readily available, preliminary tables of thermodynamic properties were issued as NBS Technical Note 130 [6] together with values from 100° to 300°K calculated from other sources. In these preliminary calculations (8) was again used. However, it was necessary to use two sets of coefficients, one set for the liquid data to 32°K and the other set for the remainder of the fluid surface, with the exception of the values between 32° and

33°K at densities greater than the critical density. In this small area not defined by the equations of state, the thermodynamic properties were smoothed with the adjacent areas by utilizing differencing techniques and empirical relations. The thermodynamic properties have now been recalculated using P-V-T relations of greater precision [7, 8, 9].

3. Neon [10] As was noted earlier, the measured data for gaseous neon are limited to temperatures of 55°K and above. In addition there are also some density data for the saturated liquid and for the saturated vapor as well as vapor pressure measurements. The generation of tabular data for neon to 25°K which includes the liquid range and pressures to 200 atm was accomplished by the utilization of corresponding states theory for predicting the vapor values, and the use of Hirschfelder's generalized equation [31] for predicting the liquid values. These calculated values, together with the experimental data were then represented by (8).

4. Nitrogen [13] Equation (8) was specifically derived for the representation of the nitrogen P-V-T data and was later used for the other fluids. The equation was fitted to approximately 500 data points for temperatures from 65° to 300°K with pressures to 300 atm, although the tabulated data are only listed to 200 atm. These same coefficients have also been used for the calculation of data to 3500 atm. A comparison with experimental data at these higher pressures indicates errors of less than 1% in density.

5. Oxygen [14] The work on oxygen is still in progress, although a preliminary report is now being prepared which includes tables of thermodynamic properties generated by (8). It is of interest to note that the first approach to the representation of this P-V-T data was to determine a set of coefficients for the new liquid data [17, 18] and a separate set of coefficients for the vapor data. In a further study, which was assumed completely unrealistic, an attempt was made to find a single set of coefficients which would represent both the liquid and the vapor data with the same accuracy as the separate equations. This attempt, however, was successful and the final coefficients for oxygen include both liquid and vapor data with an accuracy equivalent to the two separate determinations with one exception. This exception is that the equation is less accurate when extended more than 10°K below the normal boiling point for the liquid. Another equation of state is therefore used for the low temperature liquid values. Another problem with the oxygen properties was that the quantity and range of the experimental P-V-T data for the vapor is inadequate to sufficiently define this surface for fitting to (8) over the broad range of temperature and pressure to be covered. This vapor P-V-T surface was therefore first established from the nitrogen coefficients by use of the theory of corresponding states. The results were, of course, checked against the existing experimental data for oxygen.

6. Carbon Monoxide [15] The study of the properties of carbon monoxide has provided some interesting comparisons of several techniques for predicting P-V-T data. The available experimental data are for temperatures above 200°K (1.5 times

the critical) and for saturated liquid and saturated vapor. Density values were calculated with coefficients determined by the theory of corresponding states and also from Hirschfelder's generalized equation of state [31]. The results were then compared to the values predicted by Hilsenrath [23] and by Leah [22] in their respective data compilations in which each used still different calculation procedures, as well as with Keesom's P-H chart [34] which was determined by corresponding states theory using different reducing parameters. All the calculated values were also compared with the experimental data. These comparisons demonstrated that the data predicted by these various methods were essentially consistent. Equation (8) was again selected in the CEL-NBS study for generating the thermodynamic properties.

7. Argon [16] The task of compiling argon data is not as advanced as the tasks for the other fluids. A preliminary report is being prepared with tables of thermodynamic properties. Equation (8) will be fitted to approximately 500 data points for temperatures from the triple point to 300°K with maximum pressures varying from 145 to 1000 atm, respectively. Preliminary comparisons between calculated and experimental data indicate average deviations of about one-half those obtained from a similar comparison for the nitrogen data.

A word of caution in the use of (8) is necessary. It should be observed that the greatest uncertainties in P-V-T surfaces predicted by this equation are in the critical region and along the critical density. This is emphasized by considering that an equation which will reproduce both liquid and vapor values will, in general, have the

characteristics of the van der Waal equation, i. e., a cubic equation in density in the two-phase region with two of the three real roots vanishing at the critical point. Equation (8) does not, in the preceding applications, have more than one value of density along an isotherm above the critical point, but the slope of the calculated isotherm is generally flatter in the vicinity of the critical density than that of the real P-V-T surface. The density deviations that occur as a consequence of this defect in (8) have been kept small enough so that the first derivatives (and hence the values of entropy, enthalpy and internal energy) remain within acceptable tolerances. However, the second derivatives (and hence the specific heats) cannot be calculated with sufficient accuracy.

The above observations have been made primarily in the study of the new measurements for parahydrogen. Nevertheless, the utility of (8) has been clearly demonstrated in conjunction with the property calculations for parahydrogen. Because of the wide use of (8) by CEL-NBS, it is of considerable interest to note the results of a comparison of the preliminary calculations for parahydrogen using (8) with subsequent more rigorous calculations. These comparisons [8] for parahydrogen from 20° to 100°K and pressures to 340 atm indicate an average absolute error in entropy due to the variance between (8) and the real P-V-T surface of 0.34% with maximum errors of 3%. (With the exception of the area from 33° to 42°K and pressures above 10 atm, the entropy errors do not exceed 1%). The errors in density indicate an average absolute error of 0.16% with maximum errors of 4% near the critical point. (Once again, with the exception of the area near the critical point, the density errors do not exceed 1%).

The purpose of discussing various equations of state was to illustrate some of the methods used for predicting P-V-T data in the absence of measured values or to supplement and extend the range of tabular data. However, in discussing equations of state, the virial equation as introduced by Kamerlingh Onnes in 1901 must also be mentioned. With the virial equation, a power series expansion in density with temperature dependent coefficients, Onnes also defined functional relations for the first four coefficients which results in an equation of state with many coefficients. This may appear to have been suggested as a suitable expediency since many attempts to that time had failed to produce a satisfactory improvement on the van der Waal's equation. However, the virial equation is founded on firm theoretical considerations and no equation, theoretical or empirical, has yet been proposed which has a better capability of reproducing experimental data. Perhaps the particular advantage of the virial series is that statistical mechanics has provided other means of predicting the second, and with more uncertainty, even the third virial coefficient. Actually, there have been no significant theoretical equations of state in the literature for the past 30 years. Instead the theoreticians have concentrated on intermolecular potential and partition functions which may in turn be used to calculate the virial coefficients, and generally use the second virial coefficient to establish the validity of their theories. In any event, the functional form for the temperature dependence of the second and third coefficients is suggested from statistical mechanics. For the dense fluid, however, many higher order terms are necessary which can neither be satisfactorily predicted from theory nor be determined from experimental measurements. The fourth and higher order virial coefficients

obtained from fitting even the best experimental data available generally exhibit no regular temperature dependence. In general, a truncated virial expansion of three terms is only valid for densities less than one-half of the critical value. For higher densities, additional terms must be used which can only be determined empirically; as a consequence, the theoretical implications are of little value.

The recalculation of thermodynamic properties from the new density measurements for parahydrogen [7, 8] was accomplished with the use of polynomial expansions in the form of the virial equation. The experimental measurements included about 1200 P- ρ -T points along 39 isotherms. These isotherms have been represented by power series expansions of the form,

$$P = RT\rho + \sum_i A_i \rho^{(i+1)} \quad (9)$$

in which the number of coefficients, i , varied from 5 for the 100°K isotherm to 15 for the 33°K isotherm. These isothermal polynomials, which reproduce the data within the experimental accuracy, were then used to calculate pressures along isometrics which in turn were fitted by a least squares procedure to the power expansions,

$$P = A_1/T^2 + A_2/T + A_3 + A_4T + A_5T^2. \quad (10)$$

A total of 90 isometric polynomials and their first derivatives were employed to calculate the thermodynamic properties using numerical methods for the medium and high density range. An alternate method was employed in the low density range which used a truncated virial expansion with three coefficients. The second virial coefficients were then approximated by a polynomial expansion of temperature, while

the third virial coefficients were represented in three separate temperature regions by relations selected on the basis of the behavior of the first and second derivatives.

The compilation of normal hydrogen data by Woolley, Scott and Brickwedde [5] provides further examples of the P-V-T representations for the calculation of thermodynamic properties which are in contrast to the above example, inasmuch as this older work was accomplished without the benefit of a high speed digital computer. Isotherms for temperatures from 56° to 600°K were represented by,

$$\sigma = \frac{T}{T_0} \frac{1}{\rho} \log_{10} \frac{PV}{RT} \quad (11)$$

as a function of density (Fig. 3). Data above 273°K were fitted to the form $\sigma = b + c\rho$ by a least squares determination. A method of graphical interpolation was employed to obtain σ values as arguments of ρ and T for the isotherms from 56°K to 273°K.

Isotherms below 56°K were represented by,

$$\psi = \frac{T^{3/2}}{\rho} \left(1 - \frac{PV}{RT} \right) + 0.0006 \rho \quad (12)$$

as a function of density. This is illustrated in Fig. 4 for data from 29° to 56°K. Calculations from 14° to 56°K for densities less than 200 Amagat used the linear relation $\psi = A + C'\rho$. Since the data below 33°K were incomplete and lacked the precision to determine consistent isotherms, it was assumed that the linear function between ψ and ρ would continue at these lower temperatures for ρ less than 200 Amagat. The values of the intercept A were determined by smoothing the data. Values of the slope C' could not be obtained from the data in their temperature range and were therefore obtained by an extrapolation of the higher temperature data to the lower temperatures.

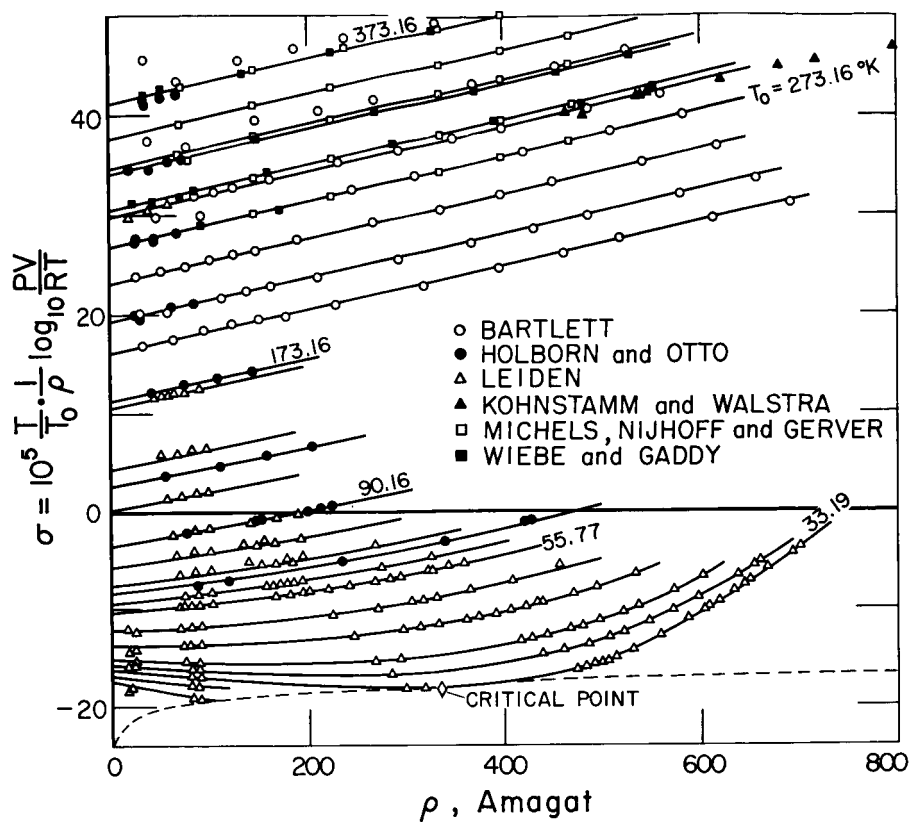


Fig. 3 P-V-T data for nH_2 as given in [5]

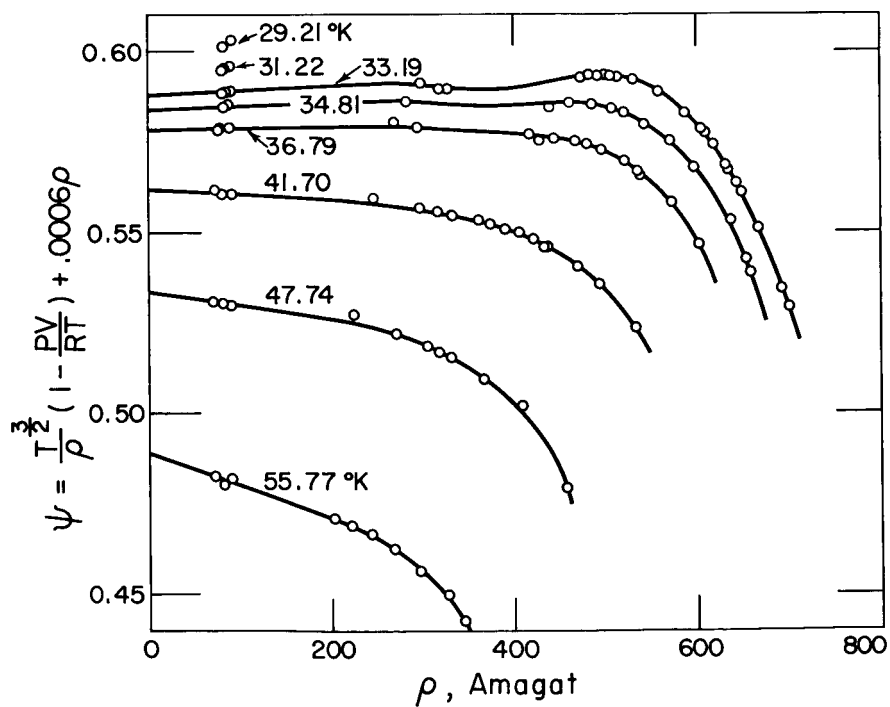


Fig. 4 P-V-T data for nH_2 at low temperatures as given in [5]

Graphical interpolations from Fig. 4 were used to obtain values of ψ with T and ρ as arguments for temperatures below 56°K and densities greater than 200 Amagat.

These are only a few examples of P-V-T representations which have been used successfully for the calculations of thermodynamic properties. Other methods, such as the use of "residuals" (where a residual is defined as the difference between a value predicted by an approximate equation of state and the measured data) as proposed by Din [35] are particularly useful, especially for graphical procedures. Smoothing of data is often accomplished by the inspection of first and second differences of tabular data. The literature suggests many procedures and techniques, and with the availability of high speed digital computers the labors of many of the best methods are now reasonable tools for the extensive calculation of thermodynamic properties.

CEL-NBS PROPERTY TABULATIONS

Reference has been made to many of the NBS publications on properties of the cryogenic fluids. Table I summarizes these documents which include tables of thermodynamic properties. A few additional references not previously cited are also included. Copies of all the documents listed are available from the NBS-Cryogenic Data Center, Boulder, Colorado. Property charts in these documents are also available separately and are also noted in Table I.

Table 1. Summary of NBS Thermodynamic Property Tables for the Cryogenic Fluids*

Fluid	Temp. Range °K	Pressure Range atm	Bibliog- raphy Reference	Properties Included			Charts Included	Remarks
				P-V-T	H,S	Saturation		
He	3 - 300	0.5 - 100	[2]	X	X	X	T-S, H-S	Charts not included, but available separately after Dec. 1963
	20 - 300	0.1 - 100	[3]	X	X		P-Z, T-S	
n-H ₂	20 - 300	1 - 100	[4]	X	X	X	see [5]	
	16 - 600	to 1678	[5]	X	X	X	T-S	
p-H ₂	20 - 300	1 - 340	[6]	X	X	X	T-S, H-S	Above 100°K, P _{max} = 100 atm. C _p , C _v , vel. of sound are included. C _v , C _p are included
	15 - 100	1 - 340	[7]	X	X	X		
	15 - 100	1 - 340	[8]	X	X	X		
	15 - 100	1 - 350	[9]	X				
	1 - 22	10 ⁻³⁸ - 1200 mmHg	[36]	X	X	X	T-S	Saturation and vapor properties
Ne	25 - 300	0.1 - 200	[10]	X	X	X	T-S	No tabular data, see [11]
	25 - 300	0.1 - 200	[11]	X	X	X	T-S, P-Z	Superseded by [10], [11]
	30 - 300	0.1 - 200	[12]	X			P-Z	
N ₂	64 - 300	0.1 - 200	13	X	X	X	T-S	Chart not included, but available separately
	10 - 77	10 ⁻³⁰ - 760 mmHg	[37]			X		Vapor pressure, heats of sublimation and vaporization
O ₂	55 - 300	0.1 - 300	[14]	X	X	X		Saturation and vapor properties
	30 - 100	10 ⁻⁷ - 1900 mmHg	[38]	X	X	X	T-S	
CO	70 - 300	0.1 - 300	[15]	X	X	X	T-S, P-Z	
A	87 - 300	0.1 - 1000	[16]	X	X	X		Vapor pressure, heats of sublimation and vaporization
	20 - 88	10 ⁻¹⁴ - 819	[39]			X		

* Available from the NBS - Cryogenic Data Center, Boulder, Colorado

BIBLIOGRAPHY

1. Bridgman, P. W., Critique of Critical Tables, Proc. Natl. Acad. Sci. U. S. 46, No. 10, 1394-1400 (1960).
2. Mann, D. B., The Thermodynamic Properties of Helium from 3 to 300 °K between 0.5 and 100 Atmospheres, Natl. Bur. Standards Tech. Note No. 154 (Jan 1962).
3. McCarty, R. D. and Stewart, R. B., An Equation of State for Calculating the Thermodynamic Properties of Helium at Low Temperatures, p. 107-17 in PROGRESS IN INTERNATIONAL RESEARCH ON THERMODYNAMIC AND TRANSPORT PROPERTIES, Second Symposium on Thermophysical Properties, Princeton Univ., New Jersey (1962), Academic Press, New York (1962).
4. Dean, J. W., A Tabulation of the Thermodynamic Properties of Normal Hydrogen from Low Temperatures to 300°K and from 1 to 100 Atmospheres, Natl. Bur. Standards Tech. Note No. 120 (Nov 1961).
5. Woolley, H. W., Scott, R. B. and Brickwedde, F. G., Compilation of Thermal Properties of Hydrogen in Its Various Isotopic and Ortho-Para Modifications, J. Research Natl. Bur. Standards 41, 379-475 (1948) RP 1932.
6. Roder, H. M. and Goodwin, R. D., Provisional Thermodynamic Functions for Para-hydrogen, Natl. Bur. Standards Tech. Note No. 130 (Dec 1961).
7. Roder, H. M., Weber, L. A. and Goodwin, R. D., Thermodynamic and Related Properties of Parahydrogen from the Triple Point to 100°K at Pressures to 340 Atm., Natl. Bur. Standards Monograph (in press).
8. Roder, H. M., Weber, L. A. and Goodwin, R. D., The Thermodynamic Functions of Parahydrogen from the Triple Point to 100°K at Pressures up to 340 atm., (NBS Report), private communication from authors.
9. Goodwin, R. D., Diller, D. E., Roder, H. M. and Weber, L. A., Pressure-Density-Temperature Relations of Fluid Para Hydrogen from 15 to 100°K at Pressures to 350 Atmospheres, J. Research Natl. Bur. Standards 67A, 173-92 (1963).

10. McCarty, R. D. and Stewart, R. B., Thermodynamic Properties of Neon, paper K-1 presented at the ninth annual Cryogenic Engineering Conference, University of Colorado and National Bureau of Standards, Boulder, Colorado August 1963.
11. McCarty, R. D. and Stewart, R. B., Thermodynamic Properties of Neon at Temperatures from 25 to 300°K and Pressures from 0.1 to 200 atm, Natl. Bur. Standards Tech. Note (in press).
12. McCarty, R. D., Stewart, R. B. and Timmerhaus, K. D., P-ρ-T Values for Neon from 27° to 300°K for Pressures to 200 Atmospheres Using Corresponding States Theory, p. 135-145 in ADVANCES IN CRYOGENIC ENGINEERING, Vol. 8, Proceedings of the 1962 Cryogenic Engineering Conference at the University of California, Los Angeles. K. D. Timmerhaus, Editor, Plenum Press, Inc., New York (1963).
13. Strobbridge, T. R., The Thermodynamic Properties of Nitrogen from 64 to 300°K between 0.1 and 200 Atmospheres, Natl. Bur. Standards Tech. Note No. 129 (Jan 1962).
14. Stewart, R. B., Hust, J. G. and McCarty, R. D., Interim Thermodynamic Properties for Gaseous and Liquid Oxygen at Temperatures from 55° to 300°K and Pressures to 300 Atm., (NBS Report), private communication from authors.
15. Hust, J. G. and Stewart, R. B., Thermodynamic Property Values for Gaseous and Liquid Carbon Monoxide from 70° to 300°K with Pressures to 300 Atmospheres, Natl. Bur. Standards Tech. Note (in press).
16. Gosman, A. L., Hust, J. G. and McCarty, R. D., Interim Thermodynamic Properties of Liquid and Gaseous Argon from 87 to 300°K with Pressures to 1000 Atmospheres, private communication from the authors.
17. Van Itterbeek, A. and Verbeke, O., Density of Liquid Oxygen as a Function of Pressure and Temperature, Cryogenics 1, No. 2, 77-80 (1960).
18. Timrot, D. L. and Borisoglebskiy, V. P., Experimental Investigation of the Density of Liquid Oxygen at -190 to -120°C and Pressures to 200 kg/cm² including the saturation curve, Inzhener. Fiz. Zhur. 4, No. 1, 3-13 (1961), translation available from Office of Technical Services, U.S. Dept. of Commerce, Washington 25, D. C., OTS 6121722.
19. Crommelin, C. A., Martinez, J. P. and Onnes, H. K., Isothermals of monatomic substances and their binary mixtures. XIX. Isothermals of neon from +20°C to -217°C, Communs. Phys. Lab. Univ. Leiden No. 154a (1919).

20. Holborn, L. and Otto, J., Über die Isothermen einiger Gase zwischen $+400^{\circ}$ und -183° , Z. Physik 33, 1-11 (1925).
21. Holborn, L. and Otto, J., Über die Isothermen von Helium, Wasserstoff und Neon unterhalb -200° , Z. Physik 38, 359-69 (1926).
22. Leah, A. S., Carbon Monoxide, p. 135-75 in THERMODYNAMIC FUNCTIONS OF GASES, Vol. 1, F. Din, Editor, Butterworths Scientific Publications, London (1956).
23. Hilsenrath, J. et al., TABLES OF THERMAL PROPERTIES OF GASES, Natl. Bur. Standards Circ. No. 564 (1955), reprinted as TABLES OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF AIR, ARGON, CARBON DIOXIDE, CARBON MONOXIDE, HYDROGEN, NITROGEN, OXYGEN AND STEAM, Pergamon Press, Oxford (1960).
24. Clayton, J. O. and Giauque, W. F., The Heat Capacity and Entropy of Carbon Monoxide. Heat of Vaporization. Vapor Pressures of Solid and Liquid. Free Energy to 5000°K from Spectroscopic Data, J. Am. Chem. Soc. 54, 2610-26 (1932).
25. Michels, A., Wassenaar, T. and Zwietering, Th. N., The Vapour Pressure of Carbon Monoxide, Physica 18, No. 3, 160-2 (1952).
26. Crommelin, C. A., Bijleveld, W. J. and Brown, E. G., Vapour Pressures, Critical Point and Triple-point of Carbon Monoxide, Commun. Kamerlingh Onnes Lab. Univ. Leiden No. 217b (1931).
27. Clusius, K. and Teske, W., Dampfdrucke und Dampfdruckkonstante des Kohlenoxyds, Z. physik. Chem. B6, 135-51 (1929).
28. Verschoyle, T. T. H., VI. The Ternary System Carbon Monoxide-Nitrogen-Hydrogen and the Component Binary Systems between Temperatures of -185°C and -215°C , and between Pressures of 0 and 225 Atm., Trans. Roy. Soc. (London) A230, 189-220 (1931).
29. de Boer, J. and Bird, R. B., Chapter 6. Quantum Theory and the Equation of State, p. 392-438 in MOLECULAR THEORY OF GASES AND LIQUIDS, by J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, John Wiley and Sons, Inc., New York (1954).

30. Kerrisk, J. F., Rogers, J. D. and Hammel, E. F., Transport Properties of He^3 , He^4 , H_2 , D_2 , T_2 , and Ne in the Liquid State According to the quantum Mechanical Principle of Corresponding States, paper K-4 presented at the ninth annual Cryogenic Engineering Conference, University of Colorado and National Bureau of Standards, Boulder, Colorado, August 1963.
31. Hirschfelder, J. O., Buehler, R. J., McGee, H. A. and Sutton, J. R., A Generalized Equation of State for Both Gases and Liquids. I., Wisconsin Univ. Naval Research Lab., Tech. Report No. WIS-OOR-15 (October 5, 1956).
32. Martin, J. J. and Hou, Y-C., Development of an Equation of State for Gases, A.I.Ch.E. Journal 1, No. 2, 142-51 (1955).
33. Yendall, E. F., Thermodynamic Properties of Neon, p. 47-64 in ADVANCES IN CRYOGENIC ENGINEERING, Vol. 4, Proceedings of the 1958 Cryogenic Engineering Conference at Massachusetts Institute of Technology, Cambridge, K. D. Timmerhaus, Editor, Plenum Press, Inc., New York (1960).
34. Keesom, W. H., Bijl, A. and Van Ierland, J. F., Log p - Enthalpy Diagrams of Carbon Monoxide and Oxygen, Communs. Kamerlingh Onnes Lab. Univ. Leiden Suppl. No. 112d (1955).
35. Din, F., editor, THERMODYNAMIC FUNCTIONS OF GASES, Vol. 1, Ammonia, Carbon Dioxide and Carbon Monoxide, Butterworths Scientific Publications, London, (1956).
36. Mullins, J. C., Ziegler, W. T., and Kirk, B. S., The Thermodynamic Properties of Parahydrogen from 1° to 22°K , Technical Report No. 1, Project No. A-593, Engineering Experiment Station, Georgia Institute of Technology, Nov. 1, 1961 (contract No. CST-7339, National Bureau of Standards, Boulder, Colorado).
37. Ziegler, W. T. and Mullins, J. C., Calculation of the Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids, Especially Below One Atmosphere. IV, Nitrogen and Fluorine, Technical Report No. 1, Project No. A-663, Engineering Experiment Station, Georgia Institute of Technology, April 15, 1963 (Contract No. CST-7404, National Bureau of Standards, Boulder, Colorado).

38. Mullins, J. C., Ziegler, W. T., and Kirk, B. S., The Thermodynamic Properties of Oxygen from 20° to 100°K, Technical Report No. 2, Project No. A-593, Engineering Experiment Station, Georgia Institute of Technology, March 1, 1962 (Contract No. CST-7339, National Bureau of Standards, Boulder, Colorado).
39. Ziegler, W. T., Mullins, J. C., and Kirk, B. S., Calculation of the Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids, Especially Below One Atmosphere Pressure. II. Argon, Technical Report No. 2, Project No. A-460, Engineering Experiment Station, Georgia Institute of Technology. June 15, 1962 (Contract No. CST-7238, National Bureau of Standards, Boulder, Colorado).